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ScienceDirect
Energy Procedia 1 (2009) 237–246
Energy Procedia
www.elsevier.com/locate/procedia

GHGT-9

Cansolv CO_2 Capture: The Value of Integration

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Abstract

If CO_2 emissions are to be reduced to control global warming, many large scale projects will need to be executed on a short term that capture and sequester the CO_2. Most studies to date have focused on CO_2 capture from power plant flue gas and concluded that the cost of CO_2 scrubbing is in itself expensive and that more mature and efficient technologies are needed.

CO_2 emission control is also complicated by the need to provide SO_2 and NOx emission control as well. Burner modifications can be used to control NOx, but other scrubbing technologies are needed to control SO_2 emissions. For high sulfur coals, limestone scrubbing is generally applied, adding to the cost of power through purchases of limestone reagent and disposal of by-product gypsum.

Cansolv has evolved amine based regenerable technologies that capture SO_2 and CO_2 and that release them in a water wet, nearly pure condition. SO_2 can be converted to sulfuric acid and CO_2 can be dried, compressed and sequestered without further treatment. Most importantly, energy used to capture SO_2 can be recycled to help capture CO_2, reducing the net energy demand of the CO_2 process. The use of these two technologies together allows power companies to use higher sulfur, lower cost fuels and reduce energy consumption rates for CO_2 capture. By-product sulfuric acid from the SO_2 scrubbing system also provides a ready source of revenue to offset scrubbing costs.

Cansolv has proven its SO_2 scrubbing technologies in commercial applications since 2002. It has operated CO_2 pilot plants at several different locations, logging over 6,000 hours of operation. The two technologies will come together in an integrated system, in a plant designed to generate 50 tons per day of CO_2, which will start up in 2009. This paper presents important design and performance advantages of these systems.

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doi:10.1016/j.egypro.2009.01.034

Amine;CO_2; SO_2; Integration; H_2SO_4; Demonstration

1. Introduction

Coal fired power plants are the world's largest point source emitters of CO_2. Depending on the sulfur content of the fuel, uncontrolled SO_2 emissions from power plant boilers can be as high as 3000 ppmv SO_2. Limestone scrubbers are widely used to control SO_2 emissions to concentrations below 35 ppmv. Unfortunately, this exceeds the mandatory requirement of conventional amine-based CO_2 capture systems for SO_2 and additional SO_2 removal is required. Cansolv has developed an amine based CO_2 removal technology that is tolerant to SO_2 and that can be combined with its SO_2 Scrubbing System to reduce overall energy requirements of the two systems.

Pure SO_2 captured by the Cansolv SO_2 Scrubbing System can be converted to a usable by-product in two ways. Firstly, it can be converted to H_2SO_4. This is likely the most attractive option for the Power Generation market. Alternately, where hydrogen sulfide is available, a Sulfur Recovery Unit can be fed SO_2 to produce additional sulfur.
If SO_2 is converted to H_2SO_4, additional heat is generated in the acid conversion step that can be used to further offset CO_2 capture energy demand.

This breakthrough technology sets a new paradigm for amine-based scrubbing technologies for SO_2 and CO_2 capture systems.

2. Business profile

Cansolv Technologies Inc. (CTI) was formed in 1997 to commercialize the Cansolv SO_2 Scrubbing System. Since 1997, CTI has continued a vigorous R&D program in order to improve the Cansolv SO_2 Scrubbing System and also to develop other gas scrubbing technologies for CO_2 recovery. At this time nine commercial Cansolv SO_2 Scrubbing Systems are in operation throughout the world in various applications, with many more in the construction and planning phase. Operating Cansolv SO_2 Scrubbing Systems have been designed to treat gases varying in flow rate from 5,000 Nm^3/hr (3,100 scfm) to 820,000 Nm^3/hr (510,000 scfm) and inlet SO_2 concentrations ranging from 500 ppmv to 12%. Resulting SO_2 emissions are as low as 10 ppmv (29 mg/Nm^3) with near zero liquid effluent.

Several Cansolv CO_2 Capture plants are also in various stages of engineering & procurement. Table 1 below describes the CO_2 commercial projects currently in progress.

Table 1 CO_2 Commercial Experience

APPLICATION	LOCATION	GAS FLOW (Nm^3/h)	INLET CO_2	CAPTURE RATE	CO_2 Capture t/day	START-UP DATE
Coal Fired Power Plant [1]	Germany	20,000	11%	90%	100	2009
Natural Gas Fired Turbine Exhaust	Norway	80,000	3%	90%	100	2009
Coal fired Blast Furnace	Japan	3,500	20%	90%	30	2010

Note 1: This plant is further detailed in section 6

1 CANSOLV CO_2 CAPTURE PROCESS HIGHLIGHTS

A successful CO_2 capture technology must be robust, proven and low cost. CTI's technologies have been developed with these constraints in mind. In addition, CTI developed its CO_2 capture technology to meet the following needs:

- **Be SO_2 compatible and/or compatible with upstream FGD**
- **Be easy to operate**
- **Have improved properties when compared to benchmark, such as:**
    - **Low regeneration energy & Low degradation of solvent**
    - **Fast kinetics: similar to primary amines**
    - **>99.9% CO_2 product purity**
    - **Minimal effluent**

2 CO_2 CAPTURE PROCESS DESCRIPTION AND PILOTING

The Cansolv System is a wet scrubbing process that uses a regenerable aqueous amine solvent to remove CO_2 from flue gases. The Cansolv Solvent is highly selective to CO_2 and balancing solvent loadings and circulation rate within the design allows complete flexibility of the system to achieve almost any desired removal rate. After absorption, the CO_2 containing solvent leaves the absorber and is regenerated using steam to produce a concentrated high purity CO_2 stream.

2.1 Extensive Research

As a proof of its viability and operability, the Cansolv CO_2 Capture process has been extensively tested for more than 6000 hours of piloting, on various flue gas streams (**Table 2**).

Table 2: Excerpt of CO_2 piloting campaign experience

Application	Date	Site	CO_2 in the gas	Removal
Natural Gas Fired boiler	March-June 2004	Paprican, Montreal, Canada	8% vol	75%
Coal fired Boiler	November 2004	Pulp Mill Boiler, US	11.5% vol	65%
Coal fired Power Plant	July – Sept 2006	SaskPower, Poplar River, Canada	12% vol	90%
Blast Furnace	April 2007 - 2008	Japan	22% vol	90%
Natural Gas Fired Boiler	May - Sept 2007	Shell-Statoil, Norway	4.5% vol	85%
Cement Kiln	Jan – Feb 2008	North America	20% vol	90% and 45%

3 OPTIMIZATION OF ENERGY: STANDALONE CO_2 CAPTURE SYSTEM

3.1 CAPEX versus OPEX

The amount of energy required by the CO_2 regeneration step is dependent on the solvent type and the system operating parameters.

While things like adequate engineering design of the regeneration column, addition of heat recovery equipment and improved mass transfer devices can all lead to certain OPEX savings, most of the energy consumption in CO_2 capture is related specifically to the amine solvent and to the way it is operated.

Solvents can therefore be customized to match the value drivers of a particular application. For example, CTI designed two different solvents DC-103 and DC-103B. As a weaker amine, DC-103 is favored by lower energy input (1.18 tons steam / ton CO_2 captured) compared to DC-103B but has higher capital cost because it requires more packing than the stronger and kinetically faster DC-103 B solvent. A rigorous optimization study is recommended for solvent selection for each industrial scenario.

Table 3 to follow shows the performance and physical expectations of the Cansolv CO_2 capture System extrapolated for a full scale system.

Table 3: Performances of Cansolv solvents (after internal heat integration[1])

Case Specifics	DC-103	DC-103B
Inlet CO_2 Concentration	~12 Vol%	~12 Vol%
CO_2 Removal	90%	90%
Specific LP Steam Consumption	< 1.2 tons/ton CO_2	< 1.35 tons/ton CO_2
Electrical Energy Requirement (pumps & equipment)	<30 HP/ton CO_2	<30HP/ton CO_2
Make-up Amine Requirement	<10%/year	<10% / year
Gas Residence Time (in mass transfer packing)	13-15 seconds	9-11 seconds
Particulate load	<30 mg/Nm^3	<30 mg/Nm^3
SO_2 ingress	35 ppmv	35 ppmv
Footprint Requirements	50-65 ft^2/MW	40-55 ft^2/MW
SO_2 ingress	35 ppmv	35 ppmv

Note 1: Internal CO_2 System heat integration only, i.e. lean amine flash recompression

3.2 Optimization trade-offs

Every case will involve an examination of site specific trade-offs in order to best optimize the cost of the capture plant with the cost of the power plant. Looking at larger, more expensive equipment may be worthwhile if the resulting operating cost savings is valued more. One such example is to decrease the temperature approach of the associated regenerator reboiler as low as realistically feasible. While the immediate impact is an increase in the price of the reboiler and much more required surface area and footprint; the potential advantage is the ability to use lower pressure steam in the regenerator. Lower pressure steam may mean less parasitic energy loss in the power cycle steam system since the steam rate (defined as $kW_{thermic}$ / $kW_{electric}$) would be higher.

3.3 Mechanical Vapor Recompression (MVR)

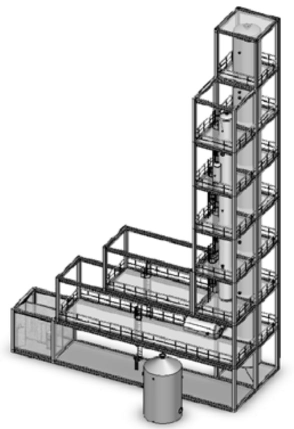
The largest and most important operating cost for implementation of an amine based CO_2 capture unit in a coal-fired power plant is the energy required for solvent regeneration. Therefore, recovery of any available energy inside battery limits can be vital to the economics of the project. Among the several engineering improvements, which are to be applied to amine based scrubbing technologies, is the Mechanical Vapor recompression (MVR) System. It derives its benefit from the fact that latent energy is available in the lean amine exiting the Regeneration section. In a regular process flowsheet, this energy is lost. By using Mechanical Vapor Recompression equipment, it allows this energy to be captured and re-introduced into the system to lower steam consumption during the regeneration step. The vapor leaving the lean amine flash tank is recompressed from 1 – 1.25 bar(a) to 2 – 2.5 bar(a) and sent back to the reboiler to reduce the consumption of fresh steam by 30%. The MVR compressor consumes energy, but the coefficient of performance is high enough that the impact of the change nets an improvement in energy demand of 15%.

Many new amine based CO_2 capture systems now being considered have only been demonstrated in 0.5 to 1.0 ton per day CO_2 capture systems. While this small size demonstration proves the chemistry and robustness of the solvent, it does not allow the absolute energy demand to be accurately measured. In addition, engineering improvements, such as MVR compression cannot be properly evaluated. CTI is entering into agreements with two coal fired power plant operators to demonstrate its technology at larger scales of operation.

4 CANSOLV 100 Ton/DAY CO_2 DEMONSTRATION PLANT

In order to prove at a large scale the Cansolv CO_2 Capture process, a large utility has purchased a Cansolv demonstration plant, to be erected and installed in Germany on a Coal Fired Power Plant. This Cansolv unit, which is in the engineering phase, will treat a slipstream inlet gas of just over 20,000 Nm^3/hr containing ~12 % CO_2 and 70 ppmv SO_2. The target CO_2 removal is 90% for a total of 100 tons of CO_2 captured per day.

This will be one of the world's largest scale amine based CO_2 capture demonstration plants. The demonstration of this technology at this scale is viewed by the operator as "an important step towards climate friendly low carbon power plant technology". He plans on using the unit to "focus on progress in terms of ecologic and economic characteristics of the post combustion capture technology" in order to drive the commercialization of the technology for the future.



Inset (Figure 1) is a preliminary engineering layout (excluding major equipment) to illustrate what the Cansolv demonstration Plant will look like. The absorber height, in this case, will be approximately 140 feet high. Overall footprint should be no more than 100 feet x 50 feet.

Figure 1: Demo Plant

5 TOLERANCE TO SO_2

Conventional primary amines used in flue gas CO_2 capture service have a significant tendency to degrade in the presence of O_2 and SO_2. Degradation causes a loss of capture capacity and eventually requires replacement of the solvent over time. While primary amines perform well in reduced gas environments, they have very low tolerance to the presence of SO_2. Specifications as low as 1 ppmv are requested by some vendors in order to offer any warranties related to removal efficiency or solvent consumption. Cost of implementation of upstream FGD reaching these low SO_2 concentrations before the CO_2 capture unit could be prohibitive. Moreover, should SO_2 concentrations exceed allowable limits in the conventional amine system, immediate reduction of CO_2 capture capacity and immediate degradation of the solvent may be expected until SO_2 concentrations return to design levels.

Cansolv CO_2 removal solvents do not present this high sensitivity to SO_2 content. For example, accelerated degradation studies showed that $SO_2/HSO_3^-/SO_3^{2-}$ concentrations as high as 2 wt% in the absorbent do not enhance the rate of formation of organic acids, which are a good indicator of the degradation rate of the amine solvent. Larger scale piloting studies deliberately fed SO_2 into the CO_2 loop. The Cansolv CO_2 removal solvents remained active for CO_2 scrubbing.

The Cansolv CO_2 Capture system uses an amine that is very similar to the Cansolv DS solvent used in the Cansolv SO_2 Scrubbing system, which has been in operation at commercial scale for over 6 years. These operating units have proven the durability of the Cansolv solvent, in large scale applications where the flue gas conditions are similar to that of conventional power plants.

5.1 SO_2 slipstream versus Amine Purification Unit

CTI's experience has shown that SO_2 in the flue gas entering the Cansolv CO_2 process does not degrade the solvent. Furthermore, more detailed studies have shown that the deliberate addition of SO_2 into the solvent can reduce its degradation rate in the presence of oxygen. SO_2 that is absorbed by the Cansolv CO_2 removal solution is present as bisulfite and sulfite. A portion of it may also disproportionate into thiosulfate and sulphate. Sulfites, are strong reductants and preferentially readily react with dissolved oxygen, mitigating the impact of oxidation on the amine. Thiosulfate is a free radical scavenger which also attenuates potential undesirable degradation reactions. All SO_2 that is absorbed by the Cansolv CO_2 removal solvent must be removed in the system's Amine Purification Unit (APU), however.

Therefore, to a certain degree, the design basis for SO_2 management systems upstream of the Cansolv CO_2 Capture system is established on the basis of an economic choice between the incremental cost of removal of SO_2 upstream of the CO_2 Absorber and removal of SO_2 from the Cansolv solvent as a heat stable salt in the APU.

If SO_2 entering the CO_2 loop is not removed, it will accumulate as non regenerable Heat Stable Salts (HSS). Eventually, HSS neutralize the Cansolv CO_2 removal solvent and reduce its ability to scrub CO_2. Cansolv's proprietary technology for HSS removal is required for all systems to manage the solution's HSS content. The APU technology is based on the use of a sodium hydroxide regenerated ion exchange resin.

So when considering a Cansolv system for CO_2 capture, one needs to re-think some of the usual notions associated with conventional CO_2 capture with amines.

In other words, the allowable concentration of SO_2 in the gas fed to the CO_2 removal system is not arbitrarily set at near zero, but is a function of the optimized cost of removal as compared to the cost of solvent to be replaced due to accelerated degradation.

Higher amounts of SO_2 entering the CO_2 solvent reduce the rate at which the solvent degrades which reduces solvent replacement costs. But the result is an increase in APU costs for higher HSS removal. The inverse is also true. So there is a balance to consider; an optimum range that maximizes the value of SO_2 ingress. As demonstrated in the figure below, the optimum SO_2 concentration range in the flue gas for a Cansolv system has been found to be 15-60 ppmv. This can be achieved by conventional scrubbing technologies and by the Cansolv SO_2 Scrubbing System. Therefore an upstream FGD system would not need to be upgraded to further remove CO_2 from the flue gas.

5.2 By-Product Waste versus End-Product Value

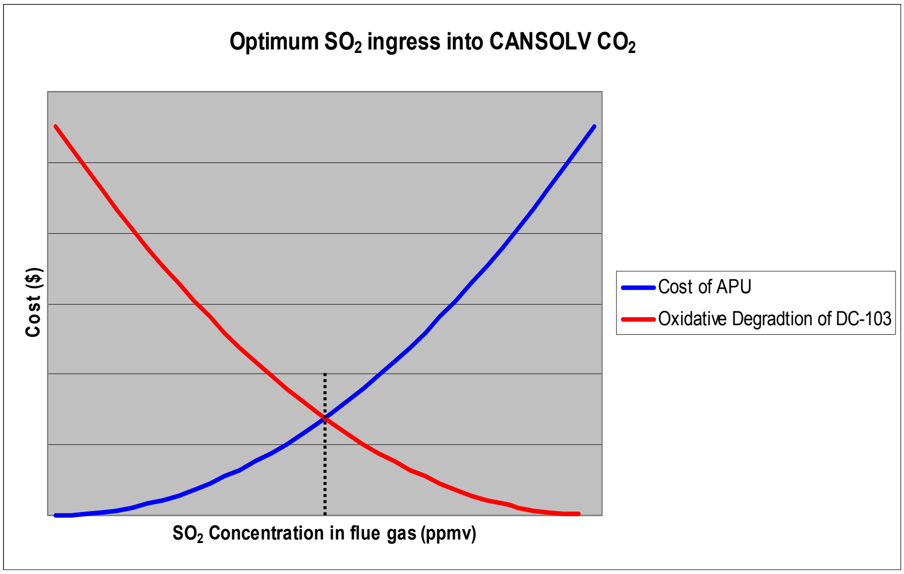
One of the challenges facing Cansolv's integrated SO_2 and CO_2 capture systems is that utilities do not historically value SO_2 as a by-product. A regenerable SO_2 Scrubbing technology requires that the user enter a new by-product market, which adds to his commercial risk and operational complexity.

In today's operating environment, several factors could lead to a shift in these mind sets:

- Recent escalating market price for sulfur and H_2SO_4 make by-product revenues significant
- Exposure to gypsum or other waste disposal liabilities may not be acceptable
- The cost of the limestone/gypsum value chain is increasing
- Post Combustion CO_2 Capture obligations may require more aggressive SO_2 removal.

Once the concept of valuing SO_2 as an End-Product is adopted, new channels of potential heat integration can also start to emerge.

5.2.1 Heat recovery from SO_2 Scrubbing



~15-60 ppmv

Being the only provider of amine based SO_2 and CO_2 removal technologies; Cansolv is able to offer the unique advantage of one integrated system to remove both pollutants simultaneously. The result is a treated flue gas stream that is released to atmosphere with the bulk of CO_2 and ALL of the SO_2 removed.

The SO_2 stripper overhead stream has a high molar fraction of water vapor. A significant amount of latent energy can be recovered from this overhead stream through the use of equipment such as a Mechanical Vapour Recompressor (MVR). This energy can be recycled from the Cansolv SO_2 system to the Cansolv CO_2 system to reduce the primary steam requirement for CO_2 capture. Up to 15% of the energy requirement in the CO_2 capture system can be obtained from the FGD system.

5.2.2 Heat Recovery from acid making

Assuming that most utilities will not have access to a stream of hydrogen sulfide (H_2S) for use in a Sulfur Recovery Unit to form elemental sulfur, the most obvious method of handling product SO_2 from Cansolv is through conversion to sulfuric acid (H_2SO_4). Sulfuric acid remains the world's most widely traded inorganic chemical and users are geographically distributed, which minimizes by-product market exposure. Recently, H_2SO_4 prices have reached all time highs, not insignificantly due to a growing population requiring more fertilizer to grow crops and food.

H_2SO_4 is produced by converting SO_2 to SO_3 in a bed of vanadium pentoxide catalyst (or equivalent). The SO_3 is then absorbed into water to produce H_2SO_4. The conversion and absorption steps are exothermic processes and as much as 1.7 tons of steam can be produced per ton of acid. This energy can be sent to the CO_2 regenerator to further offset CO_2 capture costs.
Energy saved for CO_2 capture can be valued in several ways. Reduced energy consumption can be valued either as equivalent CO_2 credits, which can generate a revenue stream, or as a decrease in the cost of the CO_2 sold into a possible EOR market. In either case, value can be generated by steam savings.

5.2.3 CO_2 Capture: A Case for Integration

Consider the following scenario where integration may be valued:

- 500 MW Bituminous Resid Fired Utility Boiler
- Fuel: 5% Sulfur, 80% carbon, balance H_2O & ash
- Flue gas: 1,250,000 SCFM flowrate, 12% CO_2, 2800 ppmv SO_2, ~122 ºF
- Utility FGD: Cansolv SO_2 Scrubbing System
- Single absorption acid plant downstream of FGD for handling/conversion of SO_2 product from Cansolv. Acid Plant Tail Gas also treated for SO_2 removal by Cansolv
- 50 psig Steam required for Cansolv CO_2 Capture: **525 metric tons/hour**

In this case implementing a Cansolv SO_2 Scrubbing system and a standard single absorption acid plant (with a heat recovery system) as the upstream FGD unit, can yield the following:

Product	Mass Flow	Additional Steam Generated	Source
SO_2 Product	15 tph (360 tpd)	90 tph	Overhead Condensers in FGD
H_2SO_4 Product	24 tph (576 tpd)	40 tph	Heat Recovery System in acid plant

In this scenario, up to 130 tons of steam per hour can be cut from the CO_2 regenerator duty, reducing the CO_2 stripping energy demand by approximately 25%.

In addition, assuming a market value of 300 USD / ton, the H_2SO_4 yields potential revenues of **more than 60 MM USD** annually.

6 INTEGRATED SO_2/CO_2 CAPTURE DEMONSTRATION UNIT

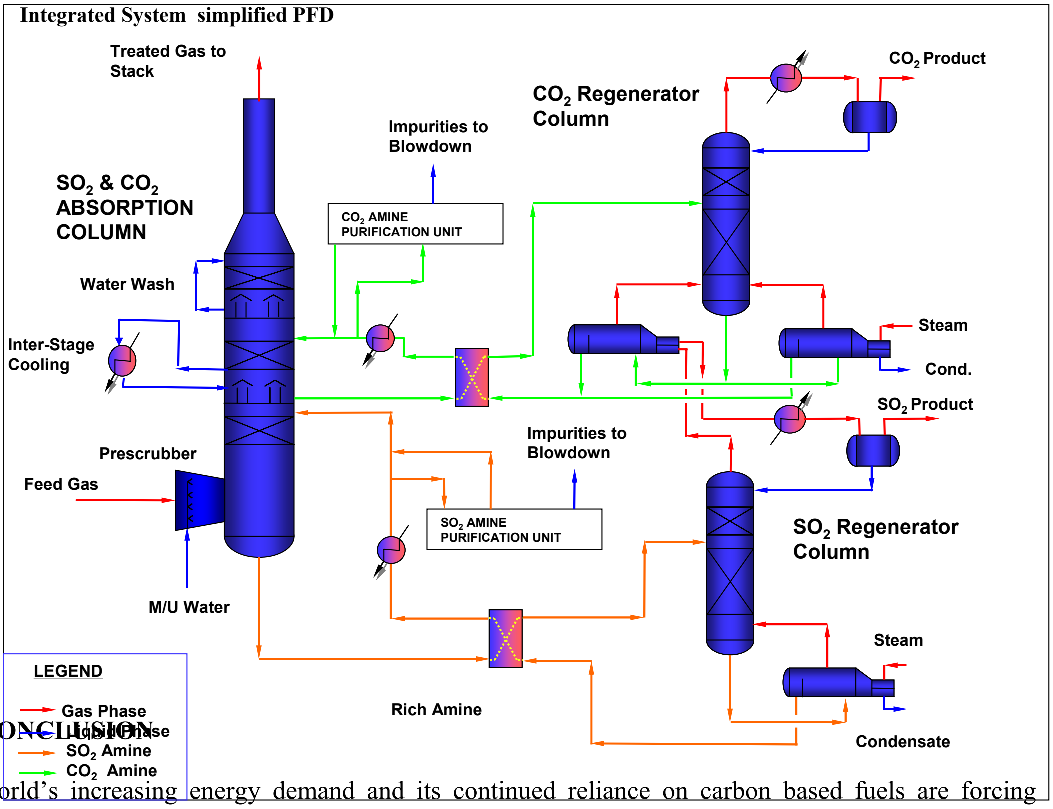
CTI is currently in the process of rolling out the world's first Integrated SO_2/CO_2 Capture System (Start-up is expected in 2009). This integrated SO_2 and CO_2 capture facility will demonstrate the benefits of recovering energy from the SO_2 system and delivering it to the CO_2 system. Upon a closer evaluation, it is evident that the two technologies are remarkably similar:

Cansolv SO_2 Control
- Diamine operating pH 4.5 to 5.5
- Regenerable ion HSO_3^-
- Stripper overheads suitable for heat recovery
- Low degradation
- Heat stable salts removed by APU
- Slips 99.99% of CO_2

Cansolv CO_2 Capture
- Diamine operating pH 9 to 10
- Regenerable ion HCO_3^-
- Stripper overheads unsuitable for heat recovery
- Low degradation
- Heat stable salts removed by APU
- Captures 99.99% of residual SO_2

This demonstration plant will be installed at a coal fired power plant and will be treating a slipstream of flue gas for simultaneous SO_2 and CO_2 removal. Cross-contamination of any of the streams (the solvent streams, for example) are not a concern since the system is designed with one common solvent management system (APU). The demonstration system will remove 50 tpd of CO_2 and will have *ZERO* SO_2 emissions. The Plant will be heat integrated (as described in section 7.2.1) and is designed to meet the following steam requirements:

- ~1.3 tons steam per ton CO_2 (without heat integration)
- < 1 ton steam per ton CO_2 (with heat integration)



7 CONCLUSION

The world's increasing energy demand and its continued reliance on carbon based fuels are forcing industry and policy makers to focus on energy efficient CO_2 removal systems. It seems inevitable that some form of penalties will soon be imposed on existing and incremental carbon emissions.

These effects will have a very significant impact on both the output of the power plant, and the overall price of electricity.

Low cost CO_2 capture systems will be justified to offset the penalties and great interest has been shown for new technologies that promise reduced CO_2 capture cost. Cansolv's approach is to offer a solution that manages SO_2, lowers parasitic energy consumption and reduces overall capital costs of these systems.

Ongoing studies on integration of our scrubbing units into power plants are leading to improved and innovative ways to tap into the existing steam cycle while exploiting the synergies of CO_2 and SO_2 capture to maximize benefit.

A combined SO_2 and CO_2 removal strategy offers significant savings in additional upstream abatement equipment, the opportunity to create new revenues from otherwise wasted by-products, as well as offers the unique advantage of turning otherwise wasted energy into precious CO_2 regeneration steam.